

On Charged Mesoscopic Metallic Bubbles *

by

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Abstract

We investigate the existence of stable charged metallic bubbles using the shell correction method. We find that for a given mesoscopic system of n atoms of a given metal and $q \ll n$ (positive) elementary charges, a metallic bubble turns out to have a lower total energy than a compact spherical cluster, whenever the charge number q is larger than a critical charge number q_c . For a magic number $(n - q)$ of free electrons, the spherical metallic bubble may become stable against fission.

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1 Introduction

Neutral and charged metal clusters consisting of a few 100 to a few 1000 atoms possibly containing a limited member (≤ 10) of positive or negative surplus charges received considerable scientific interest since 1984. At that time, when studying the formation of tiny alkali clusters out of metal vapour, an enhanced production of clusters with certain atomic numbers ($n = 8, 20, 40, 58, 92$, etc.) was observed [1, 2] and was correlated with the appearance of shell closures for the motion of the free electrons i.e. the conduction (valence) electrons in a spherically symmetric average potential for the itinerant electrons. A free electron feels an average potential which is produced by the background of positive ions, on the one hand, and by the other free electrons, on the other.

The most prominent peaks in the mass yield were shown to be due to shell closures in a spherically symmetric potential [3–8], whereas tinier details of the abundance curve

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were successfully related to secondary shell effects in axially symmetric deformed [9–11] and non-axially symmetric deformed [12] potentials.

The calculations are usually performed using the Strutinsky shell correction method [13] or the more involved self-consistent field approach [14, 15].

A large amount of beautiful experimental work [16, 17] has been performed since the discovery in 1984. The comparison between the experimental and theoretical work (see for instance Ref. 10) is in general satisfactory. The greatest part of the work has hitherto been devoted to uncharged clusters. Experiments on charged metallic clusters were performed by C. Bréchnac et al. Li_n^{+q} (n = nr of atoms, q = nr of elementary charge units) in Ref. 18 and for Sb_n^{+q} in Ref. 19. It was found that in most cases singly charged clusters are stable, i.e. their dissociation is endothermic. Clusters with a positive charge $q > 1$ are observed if the number n of constituent atoms is larger than a critical number n_b^q which depends on the system considered. Decay by fission and by evaporation of neutral or charged fragments compete with each other, the decay by fission being delayed with respect to the decay by evaporation.

Theoretical studies of the decay were published by F. Garcias et al. [20] using a semi-empirical model for the fission of multiply charged metal clusters and by D. Gross [21].

In all the theoretical studies of mesoscopic metallic clusters it was assumed that the groundstate of the cluster corresponds either to a compact spherical or to a compact deformed shape.

As we show in this paper, for large enough charge q , the state of lowest energy of a charged metallic cluster may correspond to a spherical bubble. Within the liquid drop approximation, the spherical bubble solutions turn out to be unstable versus fission. This has been shown in nuclear physics quite some time ago [22]. In a recent work [23], we found that spherical nuclear bubbles may be stabilized by shell effects. In this paper, we show that the same is true for charged metal clusters if the number of valence electrons corresponds to a closed shell.

In Section 2, we define the theoretical model and in Section 3 we present the results we obtained. In Section 4 contains a short summary and a discussion of open questions.

2 Theoretical model

For mesoscopic metallic clusters containing from 100 to more than 1000 atoms, the distribution of the positively charged ions can be approximately described by a homogeneously smeared-out density which in the simplest case is given by a step function. For a bubble with inner radius R_2 and outer radius R_1 , the density of positive ions is thus given by

$$\rho_{\text{ion}}(r) = \overset{\circ}{\rho}_{\text{ion}} \theta_0(r - R_2) \theta_0(R_1 - r) , \quad [2.1]$$

$$\theta_0(x) = \begin{cases} 1 & \text{for } x > 0 \\ 0 & \text{for } x < 0 \end{cases} .$$

The constant bulk density $\overset{\circ}{\rho}_{\text{ion}} > 0$ is usually given in terms of the radius $\overset{\circ}{r}_s$ of a sphere which contains 1 atom on the average

$$\overset{\circ}{r}_s = [3/4\pi\overset{\circ}{\rho}_{\text{ion}}]^{1/3} . \quad (2.2)$$

For a given number n of atoms, the volume of bubble layer has to be equal to the one of a compact spherical cluster of radius R_0

$$\frac{4\pi}{3}(R_1^3 - R_2^3)\overset{\circ}{\rho}_{\text{ion}} = \frac{4\pi}{3}R_0^3\overset{\circ}{\rho}_{\text{ion}} = n . \quad (2.3)$$

Consequently, the shape of the spherical bubble is determined by only one free parameter. We choose it to be the ratio

$$f := R_2^3/R_1^3 \quad (2.4)$$

between the volume of the inner hole to the volume of the entire bubble.

The conduction electrons move independently in an average potential $V(r)$ which represents the mean interaction of a given electron with all the other electrons and with the positive back ground charge $\rho_{\text{ion}}(r)$. In the Hartree-Fock approximation the single particle states $\varphi_\nu(\vec{r})$ of the electrons¹ and the corresponding single particle energies ε_ν are obtained as the selfconsistent solution of the coupled equations

$$\left[-\frac{\hbar^2}{2m}\Delta + \widehat{V}(r) \right] \cdot \varphi_\nu(\vec{r}) = \varepsilon_\nu \varphi_\nu(\vec{r}) , \quad (2.5)$$

$$\widehat{V}(r) \cdot \varphi_\nu(\vec{r}) = [V_{\text{ion}}(r) - \widehat{V}_e(r)] \cdot \varphi_\nu(\vec{r}) , \quad (2.6)$$

$$V_{\text{ion}}(r) = - \int d\vec{r}' \frac{\rho_{\text{ion}}(r')}{|\vec{r} - \vec{r}'|} , \quad (2.7)$$

$$\widehat{V}_e(r) \cdot \varphi_\nu(\vec{r}) = \sum_{\kappa \neq \nu} n_\kappa \int d^3r' \varphi_\kappa^\dagger(\vec{r}') \frac{e_0^2}{|\vec{r} - \vec{r}'|} \left[\varphi_\kappa(\vec{r}') \varphi_\nu(\vec{r}) - \varphi_\nu(\vec{r}') \varphi_\kappa(\vec{r}) \right] . \quad (2.8)$$

In (2.8), e_0 is the elementary charge and n_κ is the occupation number of the single particle state φ_κ . For temperature $T = 0$, n_κ is given by

$$n_\kappa = 1 \quad \text{for} \quad \varepsilon_\kappa < \varepsilon_F ; \quad n_\kappa = 0 \quad \text{for} \quad \varepsilon_\kappa > \varepsilon_F , \quad (2.9)$$

where ε_F is the Fermi energy. We assume that the temperature is zero.

The Hartree-Fock potential (2.8) is seen to be state-dependent mainly due to the exchange term. Usually, the exchange term is replaced by a local density approximation [3, 24]. If we neglect the exchange term altogether and suppress the exclusion of the state $\varphi_\kappa = \varphi_\nu$ in the remaining Hartree potential, we obtain

$$\widehat{V}_e(r) \varphi_\nu(\vec{r}) = \int d^3r' \frac{\rho_e^H(r') e_0}{|\vec{r} - \vec{r}'|} , \quad (2.10)$$

¹We leave away an explicit notation of the spin degrees because spin-dependent interactions are neglected.

$$\rho_e^H(r') = \sum_{\kappa} n_{\kappa} e_0 \varphi^{\dagger}(\vec{r}') \varphi_{\kappa}(\vec{r}') . \quad (2.11)$$

The solution of the remaining set of selfconsistent Hartree equations (Eqs. (2.5) with (2.6), (2.7), (2.10), (2.11)) is still a considerable technical problem. It has been carried through for instance in Ref. [3].

A considerable simplification is obtained if the selfconsistent average potential (2.6) is replaced by a phenomenological ansatz. Most of the shell structure calculations for compact metal clusters have been performed on the basis of simple phenomenological potentials, in particular the Nilsson potential [9], the Saxon-Woods potential [7, 11], and the „wine-bottle” potential [7]. It can indeed be seen from the results of Ref. [3] that for atom numbers $n \geq 40$ the selfconsistently calculated potential $V(r)$ resembles a Saxon-Woods potential and roughly even to a square well. We, therefore, felt justified to represent the average potential $V(r)$ for the case of a bubble cluster by an infinite square well with the boundaries given by the distribution of the positive ions

$$V(r) = \begin{cases} -V_0 & \text{for } R_2 < r < R_1 \\ +\infty & \text{otherwise} \end{cases} . \quad (2.12)$$

This simple choice of the shell model potential has the great advantage that the eigenfunctions of the Schrödinger equation (2.5) are linear combinations of spherical Bessel- and Neumann functions and the eigenenergies ε_{ν} are easily obtained from the boundary conditions at $r = R_{1,2}$ [23].

The well depth V_0 in (2.12) is of the order of 0.5 Ry (1 Ry = 13,6 eV). Its value is not relevant for our results because the shell correction energy (see Eq. 2.16) turns out to be independent of the constant V_0 .

We now have to determine the total energy E of the metal cluster as a function of the variable f (see Eq. (2.4)). Given the fact that the ion density $\rho_{\text{ion}}(r)$ can be considered to be constant inside the matter distribution (see (2.1)), we may write the energy of the system as a sum of the energy E_{LD} of a „liquid drop” and a „shell correction energy” E_{shell} following Strutinsky [13]

$$E_{\text{tot}} = E_{\text{LD}} + E_{\text{shell}} \quad (2.13)$$

The liquid drop energy can be written as a sum of a (negative) term proportional to the volume V of the system and a (positive) term proportional to the surface S .

Since we consider (positively) charged clusters, we have to add the electrostatic energy E_{Cb} of the sytem

$$E_{\text{LD}} = -\tau V + \sigma S + E_{\text{Cb}} \quad (2.14)$$

which turns out to be a much bigger term than in a neutral cluster.

Some authors [10] include a term proportional to the average curvature of the surface which is the 3rd term in the expansion of the energy-density functional of a leptodermous sytem in terms of $n^{-1/3}$. In the case of a bubble shape, the curvature terms arising from the inner and outer surface have opposite signs beside the fact that their absolute value is much smaller than the corresponding surface term. We omit the curvature term thereby

following Ref. [21]. Consideration of the curvature term would favour spherical bubbles as compared to compact spheres.

The „macroscopic” electrostatic energy E_{Cb} is given as a function of smooth density distributions of the positive and negative charge by

$$E_{\text{Cb}} = \frac{1}{2} \int d^3r \int d^3r' \frac{[\rho_e(r) - \rho_{\text{ion}}(r)][\rho_e(r') - \rho_{\text{ion}}(r')]}{|\vec{r} - \vec{r}'|} \quad (2.15)$$

and the shell-correction energy E_{shell} as a function of the single-particle energies ε_ν by

$$E_{\text{shell}} = \sum_{\kappa} \varepsilon_{\kappa} (n_{\kappa} - \bar{n}_{\kappa}) , \quad (2.16)$$

where the occupation probabilities n_{κ} were defined in (2.9), whereas the quantities \bar{n}_{κ} represents smooth occupation probabilities in a cluster in which the shell structure is washed out using the Strutinsky prescription [13].

In our simple phenomenological model, we represent the distribution of the positive surplus charge $[\rho_{\text{ion}}(r) - \rho_e(r)]$ by a simple ansatz: From classical electrodynamics we know that the surplus charge ought to be localized at the outer surface of the metallic bubble. We, therefore, assume the total (positive) surplus charge qe_0 to be distributed in a thin layer of thickness ε along the outer surface

$$[\rho_{\text{ion}}(r) - \rho_e(r)] = \delta\rho \cdot \theta_0(r - (R_1 - \varepsilon)) \theta_0(R_1 - \varepsilon) , \quad (2.17)$$

where

$$\delta\rho = \frac{3qe_0}{4\pi[R_1^3 - (R_1 - \varepsilon)^3]} .$$

Calculating the Coulomb energy (2.15) for this distribution we obtain

$$E_{\text{Cb}} = \frac{(4\pi\delta\rho)^2 R_1^5}{3} \left\{ \frac{1}{5} \left[1 - \left(1 - \frac{\varepsilon}{R_1} \right)^5 \right] - \frac{1}{2} \left(1 - \frac{\varepsilon}{R_1} \right)^3 \left(2\frac{\varepsilon}{R_1} - \frac{\varepsilon^2}{R_1^2} \right) \right\} . \quad (2.18)$$

Up to terms of the order of $\left(\frac{\varepsilon}{R_1}\right)^2$, this can be written

$$E_{\text{Cb}} = \frac{q^2 e_0^2}{2R_1} \left[1 + \frac{1}{3} \frac{\varepsilon}{R_1} + 0 \left(\frac{\varepsilon^2}{R_1^2} \right) \right] . \quad (2.19)$$

The term of order $\left(\frac{\varepsilon}{R_1}\right)^0$ in (2.19) represents the Coulomb energy in the limit that the surplus charge is located in an infinitely thin layer at the outer surface. One sees from (2.19) that the Coulomb energy increases if the surplus charge is distributed homogeneously in a layer of finite thickness $\varepsilon \ll R_1$. Consequently, we used the Coulomb energy in zeroth order of $\frac{\varepsilon}{R_1}$ in our calculations.

The total energy of the spherical metallic bubble has thus the form

$$E_{\text{tot}} = -\tau \cdot \frac{4\pi}{3} (R_1^3 - R_2^3) + \sigma 4\pi (R_1^2 + R_2^2) + \frac{q^2 e_0^2}{2R_1} + E_{\text{shell}}(f) . \quad (2.20)$$

Subtracting from this expression the energy of a compact spherical cluster of the same charge qe_0 and the same volume we obtain

$$\Delta E(f; q) : = \Delta E_{\text{LD}}(f; q) + \Delta E_{\text{shell}}(f; n - q) , \quad (2.21)$$

where

$$\Delta E_{\text{LD}}(f; q) = 4\pi\sigma \left(R_1^2 + R_2^2 - R_0^2 \right) + \frac{q^2 e_0^2}{2} \left(\frac{1}{R_1} - \frac{1}{R_0} \right) \quad (2.21')$$

and

$$\Delta E_{\text{shell}}(f; n - 1) = E_{\text{shell}}(f; n - q) - E_{\text{shell}}(0; n - q) . \quad (2.21'')$$

We note that the single particle potential (2.12) becomes a simple central square-well in the limit $R_2 \rightarrow 0$ (i.e. $f \rightarrow 0$). Thus the shell correction energy $E_{\text{shell}}(f = 0)$ is obtained by substituting the eigenvalues $\varepsilon_\kappa(f = 0)$ in a simple central well with infinite wall at $r = R_0$. The occupation probabilities have to be chosen in each case according to Strutinsky's prescription.

The 1st term and 2nd term of (2.21') are simple functions of the parameter f due to the relations

$$R_1 = R_0 \cdot \left(\frac{1}{1 - f} \right)^{1/3} , \quad (2.22)$$

$$R_2 = R_0 \cdot \left(\frac{f}{1 - f} \right)^{1/3} . \quad (2.22')$$

The radius R_0 of the compact spherical cluster is related to the number of n of atoms by

$$R_0 = \overset{\circ}{r}_s n^{1/3} \quad (2.23)$$

with the radius parameter given in (2.2).

The surface tension σ and the radius $\overset{\circ}{r}_s$ of the Wigner-Seitz cell are thus the only parameters which specify a given metal in our model.

The difference $\Delta E_{\text{LD}}(f; q)$ between the LD-energies of the compact cluster and the bubble (Eqn. (2.21')) is seen to consist of a positive term describing the increase of the surface energy and a negative term which represents the reduction of the repulsive Coulomb energy. As far as the „macroscopic” part of the energy is concerned, a preference for the bubble geometry may only occur through the reduction of the Coulomb energy which increases with the surplus charge q of the metal cluster. For a given metal and a given „size” n of the cluster there will thus be a critical value q_c of the charge at which the (spherical) bubble becomes the configuration of lower energy. It will depend on the type of the metal (i.e. on the value of the surface tension σ and the radius parameter $\overset{\circ}{r}_s$) whether the cluster is still stable versus fission or emission of atoms at this value of the charge.

The difference ΔE_{shell} of the shell correction terms can be positive or negative. If the number $(n - q)$ of valence electrons happens to be a magic number for the bubble geometry, and not for the compound spherical form, ΔE_{shell} will be a negative number and thus favour the formation of a bubble a.v.v.

The question whether, for given charge, the bubble has a lower energy than the compact sphere, depends sensitively on the value of the surface constant σ and the radius parameter $\overset{\circ}{r}_s$. More precisely, it depends on the "fissility" parameter which is defined to be the ratio of the Coulomb energy E_{Cb} and twice the surface energy E_S . The factor 2 is inserted in order to retain the definition used in nuclear physics:

$$X = \frac{E_{\text{Cb}}(f)}{2E_S(f)} = \frac{q^2 e_0^2}{16\pi\sigma \cdot R_1(R_1^2 + R_2^2)} = X_0 \cdot \left(\frac{1-f}{1+f^{2/3}} \right), \quad (2.24)$$

with X_0 , the fissility parameter of a compact sphere, being defined by

$$X_0 = \frac{E_{\text{Cb}}(f=0)}{2E_S(f=0)} = \frac{q^2 e_0^2}{16\pi\sigma \overset{\circ}{r}_s^3 n}. \quad (2.25)$$

The difference ΔE_{LD} between the LD-energy of the spherical bubble and of the compact spherical cluster (see (2.21')) measured in units of $2E_S(f=0)$ is given by the function

$$F := \frac{\Delta E_{\text{LD}}(f; q)}{2E_S(f=0)} = \frac{1}{2(1-f)^{2/3}} [1 + f^{2/3} - (1-f)^{2/3}] - X_0 [1 - (1-f)^{1/3}]. \quad (2.26)$$

of the hole parameter f ($0 \leq f < 1$), the 1st term on the r.h.s. is positive and the 2nd term is negative. Clearly, for large enough X_0 , the function F becomes negative, i.e. the bubble shape corresponds to a lower energy. The stationarity condition

$$\frac{\partial F}{\partial f} = 0 \quad (2.27)$$

has the explicit form

$$1 + f^{1/3} - X_0 f^{1/3}(1-f) = 0. \quad (2.28)$$

Solving Eq. (2.28) one can find that the metallic cluster with charge $q \cdot e_0$ and the atom number n have their lowest energy for a spherical bubble shape if the fissility parameter $X_0 < X_0^{cr} = 3,4$.

A crucial question is the dependence of the total energy on deformation: It can be easily shown that the LD-energy of a bubble decreases as a function of deformation because the decrease of the repulsive electrostatic energy turns out to be greater than the increase of the surface energy. A spherical bubble may, however, be stabilized against deformation by shell effects. If the $(n - q)$ valence electrons of the charged metal bubble correspond to a closed shell configuration in the spherically symmetric potential (2.12), the shell energy yields an additional binding of a couple of eV. As one deforms the bubble the absolute value of this negative shell energy decreases as a function of deformation. In this way a barrier against fission is produced. The calculation of the total energy of the bubble as a function of the deformation implies that we determine the eigenvalues in a deformed bubble potential. This is a difficult task if we were to tackle it in full generality. There is, however, a family of deformed shapes which can be transformed into

a spherical shape by a scaling transformation. For this "scaling model", it is relatively simple to calculate the eigenvalues:

Assume that the outer (S_1) and inner (S_2) surface of the deformed bubble are concentric spheroids with the half-axes $a_{1(2)}$ and $c_{1(2)}$

$$S_{1(2)} : \frac{x^2 + y^2}{a_{1(2)}^2} + \frac{z^2}{c_{1(2)}^2} = 1 \quad (2.29)$$

enclosing the constant volume $\frac{4\pi}{3}(R_1^3 - R_2^3)$

$$R_0^3 = R_1^3 - R_2^3 = a_1^2 c_1 - a_2^2 c_2 . \quad (2.30)$$

An infinite square well with the boundaries (2.29)

$$\hat{V}(x, y, z) = -V_0 \eta_0(\vec{x}) , \quad (2.31)$$

where

$$\eta_0(\vec{x}) = \begin{cases} 1 & \text{for } \vec{x} \in \text{volume } \Omega \text{ enclosed by } S_1 \text{ and } S_2 \\ -\infty & \text{otherwise} \end{cases}$$

transforms into a simple spherically symmetry potential of the type (2.12) which depends on the scaled variable

$$\xi = \lambda x; \quad \eta = \lambda y; \quad \zeta = \mu z \quad (2.32)$$

or the corresponding polar variables ρ, ϑ, φ

$$\xi = \rho \sin \vartheta \cos \varphi; \quad \eta = \rho \sin \vartheta \sin \varphi; \quad \zeta = \rho \cos \vartheta . \quad (2.32')$$

The 2 scaling parameters λ, μ are related to each other by the constraint (2.25) which takes the form

$$\lambda^2 \mu = 1 . \quad (2.33)$$

Thus they can be expressed by a single deformation parameter. Using the deformation parameter δ introduced by S. G. Nilsson in Ref. [25] the scaling parameters are given as a function of δ by

$$\lambda = \left(\frac{1 + \frac{2}{3}\delta}{1 - \frac{4}{3}\delta} \right)^{\frac{1}{6}} , \quad \mu = \left(\frac{1 - \frac{4}{3}\delta}{1 + \frac{2}{3}\delta} \right)^{\frac{1}{3}} . \quad (2.34)$$

In the scaled variables, the Schrödinger equation takes the form

$$(\hat{H}_0 + \hat{H}_1)\varphi_\nu = \varepsilon_\nu \varphi_\nu . \quad (2.35)$$

The hamiltonian \hat{H}_0 is spherically symmetric in the ξ, η, ζ coordinates

$$\hat{H}_0 = -\frac{\hbar^2}{2M_\delta} \Delta_{\xi\eta\zeta} + V(\rho) , \quad (2.36)$$

where $\Delta_{\xi\eta\zeta}$ is the Laplacian operator in ξ, η, ζ space and

$$M_\delta = M(1 + \frac{2}{3}\delta)^{\frac{2}{3}}(1 - \frac{4}{3}\delta)^{\frac{1}{3}} . \quad (2.37)$$

The scaled square well potential is now spherical

$$V(\rho) = \begin{cases} -V_0 & \text{for } R_2 < \rho < R_1 \\ +\infty & \text{otherwise} \end{cases} . \quad (2.38)$$

The term \hat{H}_1 in (2.31) represents the deformation dependent part of the hamiltonian

$$\hat{H}_1 = \frac{2}{3}\delta \frac{\hbar^2}{2M} \left(2\frac{\partial^2}{\partial\zeta^2} - \frac{\partial^2}{\partial\xi^2} - \frac{\partial^2}{\partial\eta^2} \right) . \quad (2.39)$$

For determining of the stability of spherical bubble with respect to elongation, we only need to consider small deformations δ . Consequently, we may treat \hat{H}_1 as a perturbation. This means that the single-particle energy ε_ν can be approximately obtained as a function of the eigenenergies $\overset{\circ}{\varepsilon}_\nu$ and eigenfunctions $\overset{\circ}{\varphi}_\nu$ of the Hamiltonian \hat{H}_0 as

$$\varepsilon_\nu \approx \overset{\circ}{\varepsilon}_\nu + \langle \overset{\circ}{\varphi}_\nu | \hat{H}_1 | \overset{\circ}{\varphi}_\nu \rangle . \quad (2.40)$$

For larger deformations, one has to diagonalize \hat{H}_1 in the basis of the s.p. states $\overset{\circ}{\varphi}_\nu$. In all the results shown in Section 3, the eigenvalues ε_ν were determined by diagonalization of \hat{H}_1 in a sufficiently large subspace of s.p. states $\overset{\circ}{\varphi}_\nu$.

The matrix-elements of \hat{H}_1 can be easily evaluated using the following artifice

$$2\frac{\partial^2}{\partial\zeta^2} - \frac{\partial^2}{\partial\xi^2} - \frac{\partial^2}{\partial\eta^2} = \frac{1}{8} [\Delta_{\xi\eta\zeta}, [\Delta_{\xi\eta\zeta}, 2\rho^2 P_2(\cos\theta)]] = \frac{1}{8} \left(\frac{2M_\delta}{\hbar^2} \right)^2 [\hat{H}_0, [\hat{H}_0, 2\rho^2 P_2(\cos\theta)]] . \quad (2.41)$$

where P_2 is the Lagrange polynomial. Simple algebra leads to the expression

$$\langle \overset{\circ}{\varphi}_\nu | \hat{H}_1 | \overset{\circ}{\varphi}_\mu \rangle = \frac{\delta}{6} \left(\frac{2M_\delta}{\hbar^2} \right) (\overset{\circ}{e}_\nu - \overset{\circ}{e}_\mu)^2 \langle \overset{\circ}{\varphi}_\nu | \rho^2 P_2(\cos\theta) | \overset{\circ}{\varphi}_\mu \rangle , \quad (2.42)$$

The matrix elements of ρ^2 were evaluated numerically, while the matrix elements of spherical harmonics are expressed in terms of Clebsch-Gordan coefficients.

3 Results

The calculation was performed for metallic agglomerates of sodium (*Na*) and of antimony (*Sb*). The liquid drop parameters are the same as in Ref. [21] where the fission of charged clusters was discussed. For *Na* clusters we have used the set

$$\overset{\circ}{r}_s = 2.070 \text{ \AA} , \tau = 0.03017 \text{ eV} , \sigma = 0.01894 \text{ eV}$$

and for *Sb* clusters

$$\bar{r}_s = 1.130 \text{ \AA} , \tau = 0.4552 \text{ eV} , \sigma = 0.02474 \text{ eV} .$$

The results for the charged sodium clusters are presented in Fig. 1. The number n of atoms in clusters vary from 700 to 10000, while the charge number q changes from 30 to 200. The liquid drop estimate of the binding energy (E_{LD} , Eq. 2.1), the energy gain (ΔE_{LD} , Eq. 2.21') with respect to the energy of a compact spherical cluster, the fissility parameter (X , Eq. 2.24) and the equilibrium hole fraction (f , Eq. 2.4) are drawn. It is seen in the Fig. 1 that only massive and relatively highly charged *Na* clusters favour the bubble solution. The average energy gain is around 0.3 eV per atom. The hole fraction parameter f varies from 0.3 to almost 0.9 and the hole in the bubble is larger the higher is the charge of the cluster. Unfortunately the fissility parameter X is always larger than one. This means that there is no fission barrier in the liquid model and there is a little hope that the shell effect is large enough to stabilize the sodium bubble.

A more optimistic situation exists for the *Sb* clusters, which have a smaller Wigner-Seitz radius constant. In Fig. 2 we plotted analogous results as in Fig. 1. One can see that already small and not highly charged clusters prefer the bubble configuration. The energy gain with respect to the compact shape could even reach 1 eV per atom, also the binding energies per atom are few times larger than for *Na* bubbles. But the fissility parameter X is here also larger than one. One can conclude from the LD results presented in Figs 1 and 2 that within the LD model stable bubble clusters are rather improbable. Only the shell effects may stabilize them with regard to fission.

The electronic scheme obtained for the infinite spherical square well potential (2.12) is plotted in Fig. 3 as a function of the hole fraction f (2.4). The energy unit used takes into account that the eigenvalues of the infinite square well scale with $n^{-2/3}$. The radius constant for *Sb* is used here. It is seen in the figure that for larger f the orbitals with the node number $n > 1$ corresponds to much higher energies than those with $n = 1$ and the levels are well separated from the others. This effect leads to strong shell effects. A similar tendency was also observed in the shifted harmonic oscillator [23]. New magic numbers corresponding to the orbitals with $l=0, 1, 2, 3, \dots$ are found:

$$\mathcal{M}_{bubb.} = 2, 8, 18, 32, 50, 72, 98, 128, 162, 200, 242, 288, 338, 392, 450, 512, 578, 648, \dots$$

These magic numbers are quite different from those observed in the compact spherical clusters [26] :

$$\mathcal{M}_{comp.} = 2, 8, 20, 34, 58, 92, 138, 168, 254, 338, 438, 440, 542, 556, 676, \dots$$

The Strutinsky shell correction energy for the *Sb* bubble cluster with the hole fraction $f=0.7$ is plotted as a function of n in Fig. 4. The shell correction energy for a magic number of valence electrons in the bubble cluster is negative and reaches even -3 eV for $n=648$. The magnitude of the shell correction is comparable with that for supershells for heavy clusters with $1074 \leq n \leq 3028$ discussed by Brack in Ref. [26]. Such a huge shell effect for magic clusters should protect them against fission. It can be seen in Fig. 5,

where the fission barrier for the magic bubble cluster ${}_{210}\text{Sb}^{+10}$ is analysed. In the upper l.h.s. part of Fig. 5, the liquid drop energy is drawn as a function of the hole fraction f . A pronounced bubble minimum is observed at $f \approx 0.4$. The liquid drop part of the energy at $f=0.4$ is plotted as a function of deformation parameter δ in the upper r.h.s. part of Fig. 5. As one can expect there is no fission barrier in this case. The two lower graphs represent the shell energy (2.16) and the fission barrier being the sum of the LD part and the shell correction (2.13) as a function of δ . It is seen that $E_{\text{shell}}=-2,7$ eV for spherical configuration and its magnitude decreases with deformation and oscillates. This effect produces a pronounced fission barrier which makes fission of ${}_{210}\text{Sb}^{+10}$ rather improbable.

4 Summary and discussion

We have investigated the shell correction energy of charged spherical bubble clusters. The lower limit of mass and charge numbers, where bubble clusters begin to exist depends sensitively on the choice of the LD parameters. The investigation shows that promising candidates for bubble structure are *Sb* clusters with a magic number of itinerant electrons in the charged agglomerate. The charge number is found to be a fraction of 0.04 to 0.15 of the atom number. The *Na* cluster should contain large atom number, preferably a few thousands and they should be highly charged ($q \approx 100$).

We have found strong shell effects which may give rise to shell energies of up to -4 eV for certain magic numbers. By calculating the LD-energy for deformed bubbles and the deformation dependence of the shell effect, we found that the fission barriers are of the same order of magnitude as the shell-correction energy for the spherical bubble solution. In favorable cases of magic numbers, this is sufficient to reduce significantly the probability for spontaneous fission. The origin of the shell effects is the high degeneracy of orbitals with large angular momentum and the rapid energetic increase of radial oscillation modes as a function of increasing bubble radius.

We expect that similarly big shell effects could exist in the clusters in which the outer layer from other material is added. If would exist the potential barrier between the inner and outer material then the electrons in the outer metallic layer could feel the magic numbers like those found for the bubble cluster. It would be a great challenge for experimentalists to produce (by epitaxy?) such objects.

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Figures captions:

1. Liquid drop estimate of the binding energy (E_{LD} , Eq. 2.1), energy gain (ΔE_{LD} , Eq. 2.21') with respect to the energy of a compact spherical cluster, fissility parameter (X , Eq. 2.24) and the equilibrium hole fraction (f , Eq. 2.4) for the charged ($q \cdot e_0$) sodium cluster with the bubble structure as function of n .
2. The same as in Fig. 1 but for charged clusters of antimonium.
3. Electronic level scheme as a function of the hole fraction $f = (R_2/R_1)^3$ for the infinite spherical square well (2.12). The energy unit used takes into account that the eigenvalues of the infinite square well scale with $n^{-2/3}$. The radius constant for Sb cluster is used here.
4. Shell correction energy for the Sb bubble cluster with the hole fraction $f=0.7$ as a function of n .
5. Liquid drop energy of ${}_{210}Sb^{+10}$ as a function of the hole fraction f (upper l.h.s. figure) and the deformation parameter δ (upper r.h.s). The two lower graphs represent the shell energy (2.16) and the fission barrier (2.13) as a function of δ .

Figure 1:

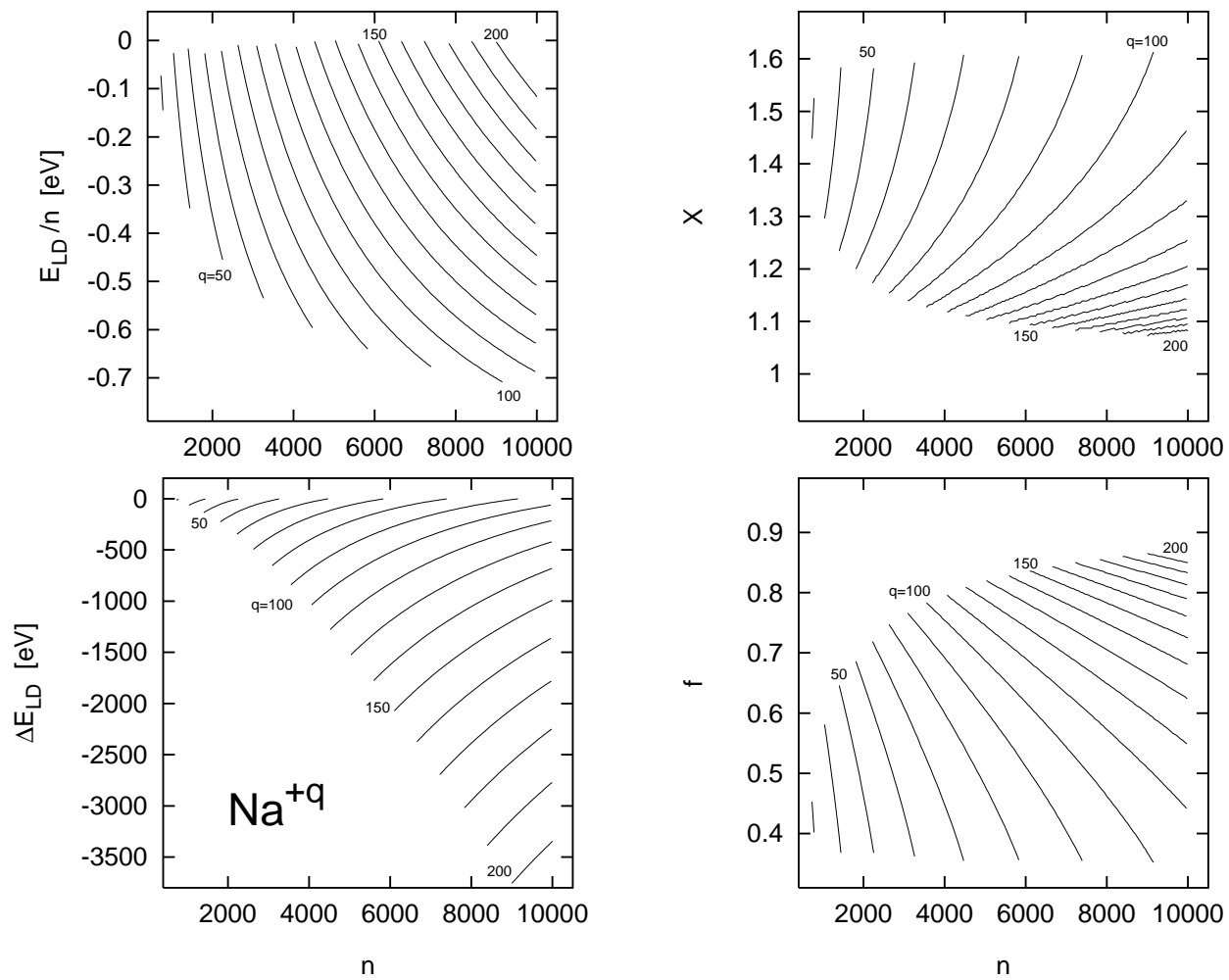
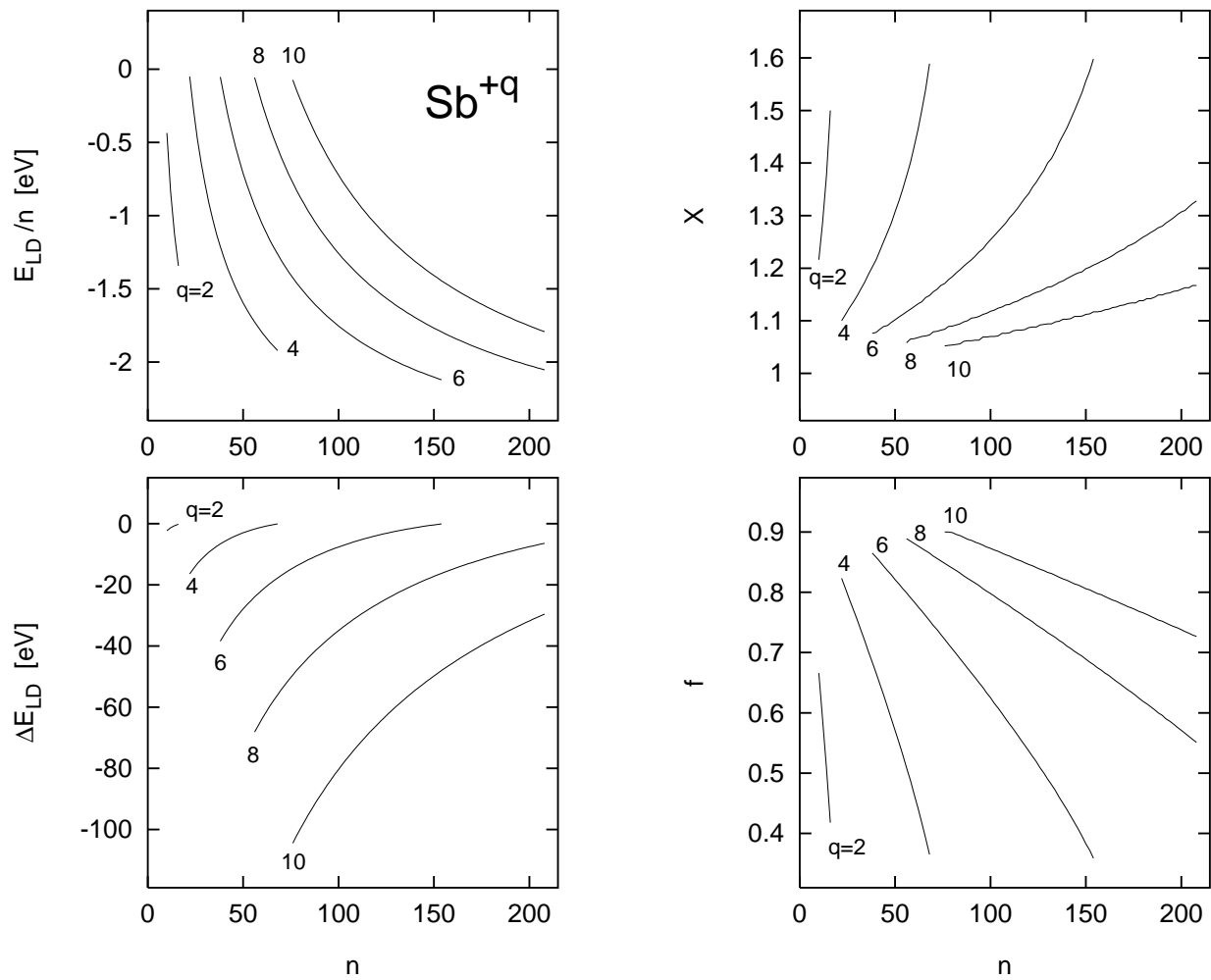


Figure 2:



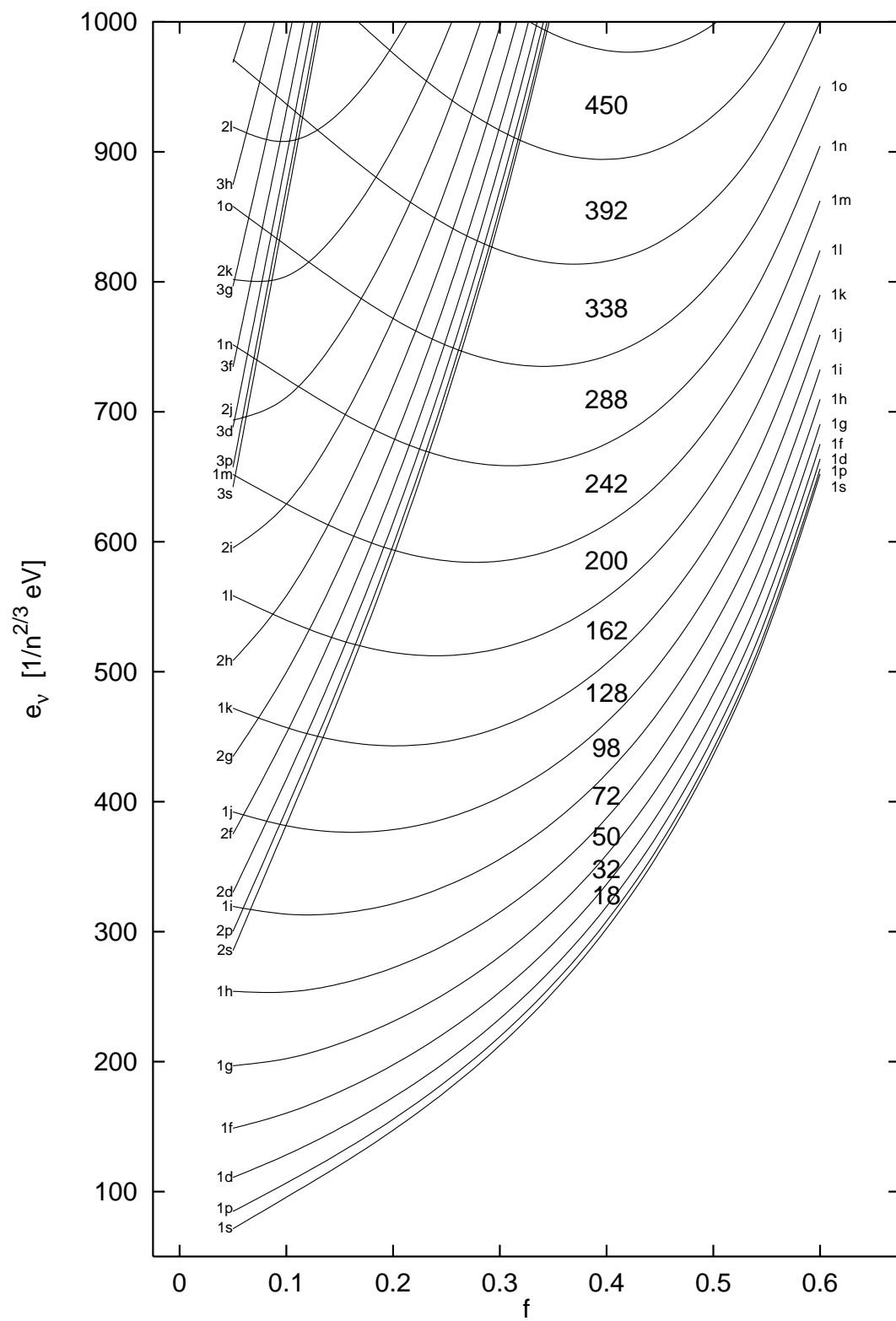


Figure 3:

Figure 4:

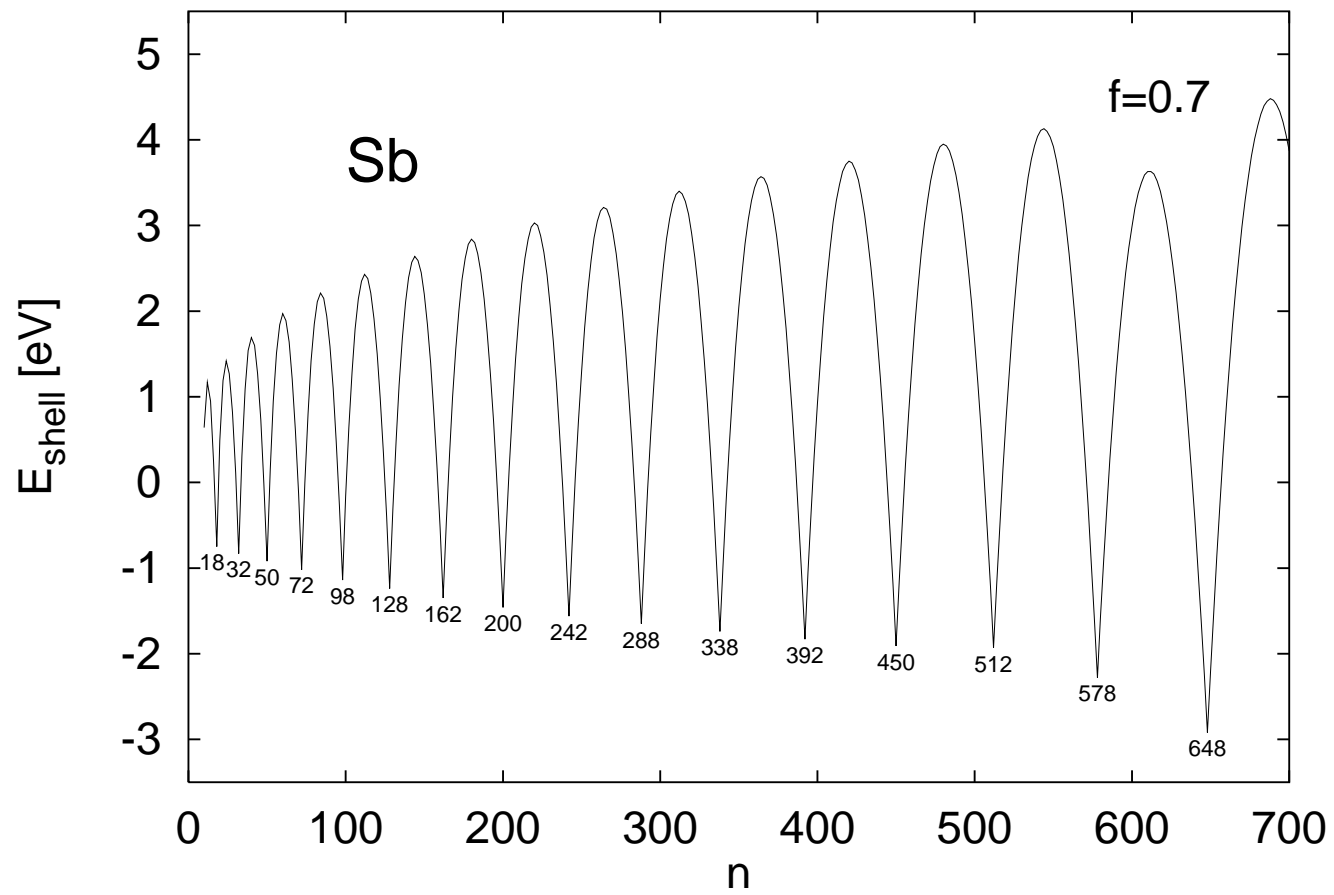


Figure 5:

